DOE Hydrogen Program

Reversible Liquid Carriers for an integrated Production, Storage and Delivery of Hydrogen

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PD23

Overview

Timeline

- Start: Date 8/2005
- Project end March 2011(tentative)
- 30% Complete
- Funding delayed FY'06

Budget

- Total project $4,131,138
  - DOE share (75%)
  - Contractor share (25%)
- Funding received in FY07:$900,000
- Funding for FY08 $834,583

Barriers

- Barriers addressed

E. Solid and Liquid Carrier Transport

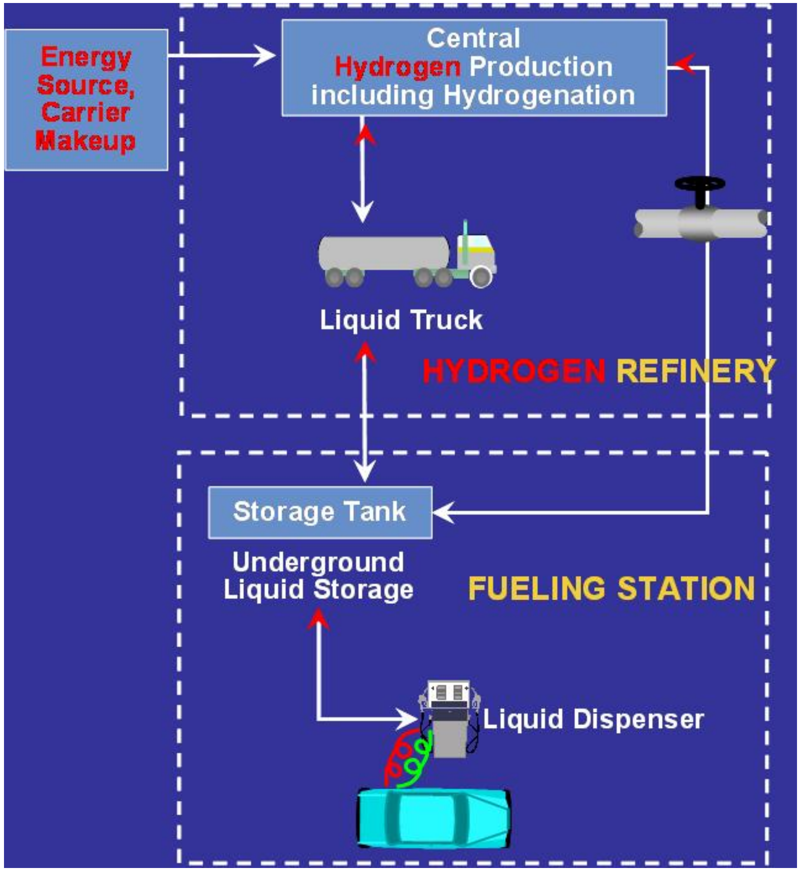
A. Hydrogen/Carrier and Infrastructure Options Analysis

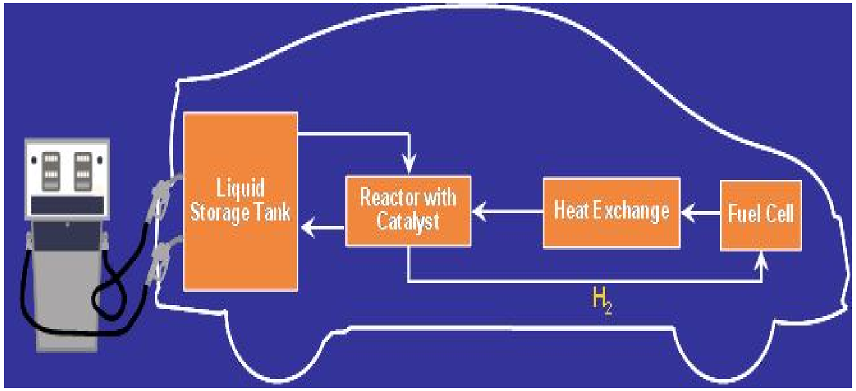
F. Hydrogen Delivery Infrastructure Cost

Partners

- Pacific Northwest National Laboratory/Battelle
- United Technologies Research Corporation (UTRC)
- OEM (to be finalized)

Objectives





- Enable Liquid Carrier concept
  - Prototype dehydrogenation reactor
  - Economic study to determine concept’s viability

Approach

- Overall Tasks
  1. Develop a conceptual design and fabricate a laboratory prototype dehydrogenation reactor/heat exchange system to deliver H_2
  2. Study of economics of H_2 liquid carrier delivery

- Reactor Design
  - Measure performance of packed bed reactor
  - Devise advanced reactor designs
    - APCI single channel
    - *PNNL multichannel*
  - *OEM partner and UTRC integration*
  - *Choose final design*
  - *Build and test prototype*
- Perform the economic study

Milestones

Month/Year	Milestone or Go/No-Go Decision
18 months after start of microchannel reactor work Original:June-07	Go/No-Go decision: Reactor Configuration for prototype reactor.
May-07	Milestone: Complete Economic Study

Dehydrogenation Reactor Challenges

- Gas flow rate large and variable
  - 50 KW ~1 gm/min. H_2, 11.2 Std Liters/sec.
  - 1 liter of liquid generates 600 L of gas at complete conversion
  - Demand varies
- Carrier molecule large relative to pore size
- Heat Load Significant (~6 Kcal/min.)
  - Waste heat from Fuel Cell limits ΔT (mobile)
- Mass transfer is desorption--normal correlations may not be usual
- Experimental Program needed

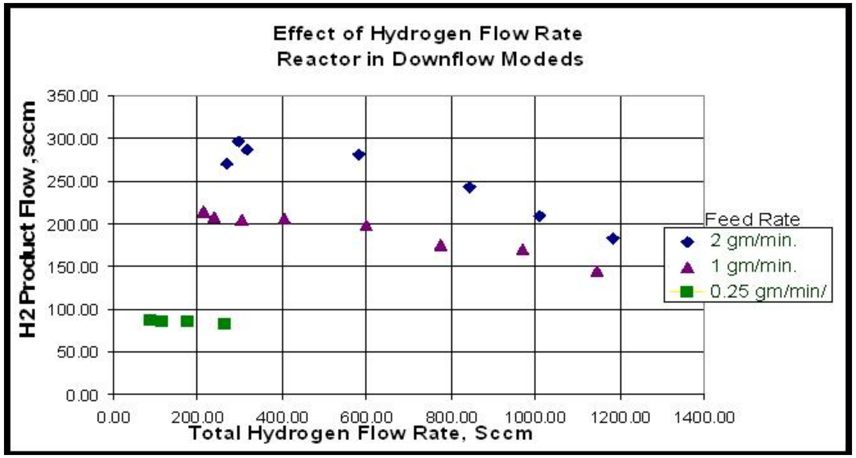
Packed Bed Reactor Performance

- N-Ethylcarbazole/Pd model system
  - Modest Productivity
    - 220 ^{o}C- 0.8 l/min. 60 cc (2.5 gm Pd, 60%)
  - Simple separation of hydrogen with quality potentially adequate for FC
  - Hydrogen purity sustained over ~15 cycles Pd catalyst
  - Stability of catalyst and liquid demonstrated over >400 hours in reactor (many years of use in car)

Conclusion: Packed bed reactor system possible

Flow and Mass Transfer Limits

- **Modest increases in hydrogen flow rates decreases productivity.**
- **Low Effectiveness Factor (using kinetic model as baseline)**
  - **ή = 0.08 measured**
  - **ή = 0.1 correlations**
  - **Pellet diameter (2 mm) limits diffusion**
- **Conclusion: Packed bed reactor system will be inefficient.**

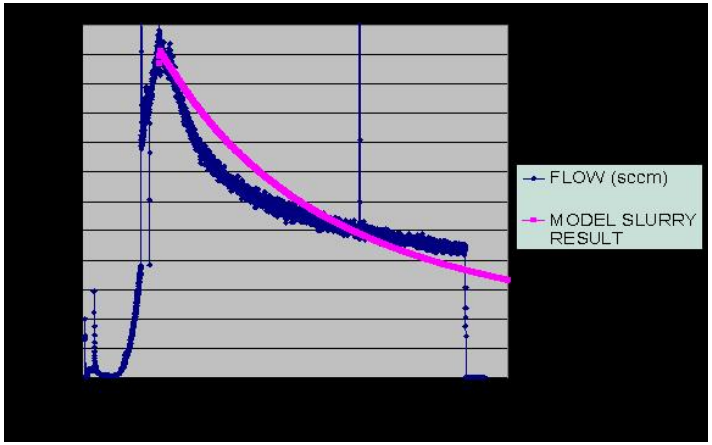


Advanced Designs-Monolith Thin Film Catalyst Development

- **FeCrAlloy substrate (50 μ) coated with catalyst gives thin catalyst film (25 μ)**
- **Good Productivity (~0.15 gm Pt) using continuous reactor**
  - **0.8 l/min, @ 250 ^{o}C 65% conversion**
  - **85% conversion with 2 passes**
- **Selectivity**
  - **Pd gives same high selectivity >99% as packed bed reactor**
- **Conclusion: Thin film catalyst can be effective.**

Thin Film Catalyst Efficiency

- Slurry reactor measures intrinsic catalyst activity
- CatRak measures thin film catalyst activity
- Model relates intrinsic activity to wash coat
- Conclusion: High catalyst efficiency demonstrated but mass transfer limits conversion

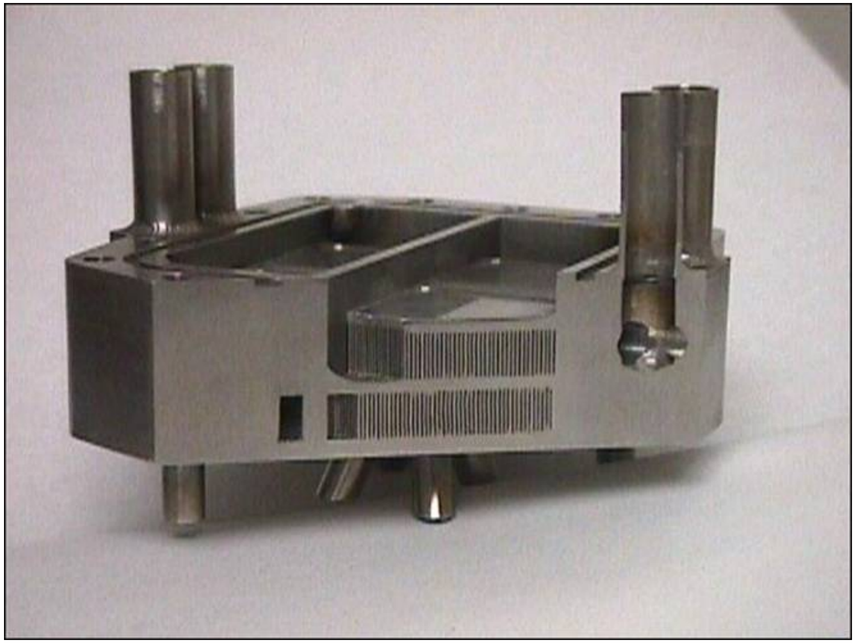


Monoliths in Continuous Flow Reactor

- Flow Fluctuations Found
  - Thermocouples showed temperature fluctuations which can only be explained flow instabilities.
  - Increasing gas flow decreased conversion indicating flow irregularities
- Very recent literature indicates microchannel flow instability caused by generation of large flow gas at wall.
- Thus, feeding monolith in tube can give stability problems and fluctuations in conversion from channel-to-channel for dehydration.

Microchannel Reactor Rationale

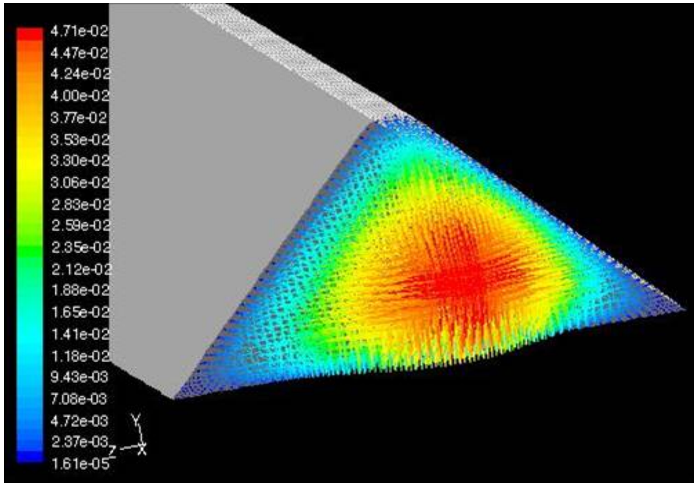
- **Uses effective thin–film catalyst**
- **High rate heat transfer possible**
- **Large number of identical channels allows**
  - **Mass production of large number of reactors for filling stations or automobiles**
  - **Accommodation of varying demand and complete conversion turning on desired number of reactors to meet demand requirement**



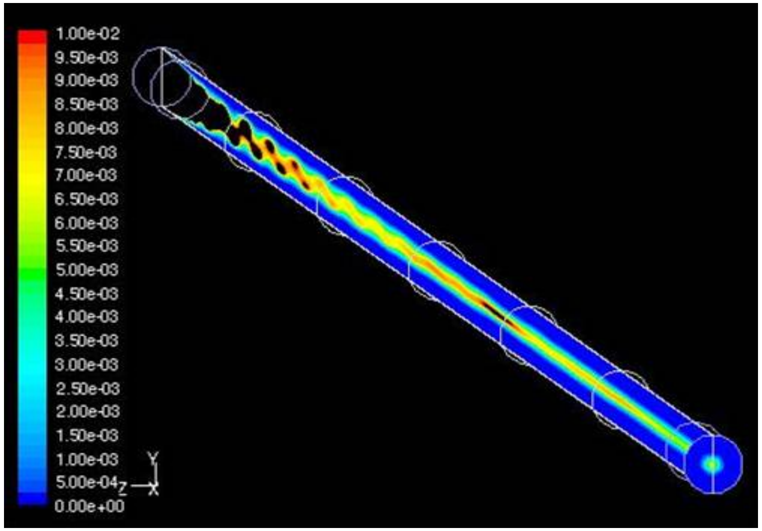
Battelle 50 kW combustor-gasoline vaporizer.
Full size unit, ~ 13 cm at longest dimension

Flow Characteristics of Single Channel

- CFD Simulations
  - Liquid simulation shows slow flow at corners of triangular tubes
  - Adding H_2 from walls causing drying out of surface
  - Circular tubes give better flow, but catalyst could “dry out” at high gas flow rates.
- Conclusion: Multichannel microreactors could be viable but need design expertise for successful scaleup

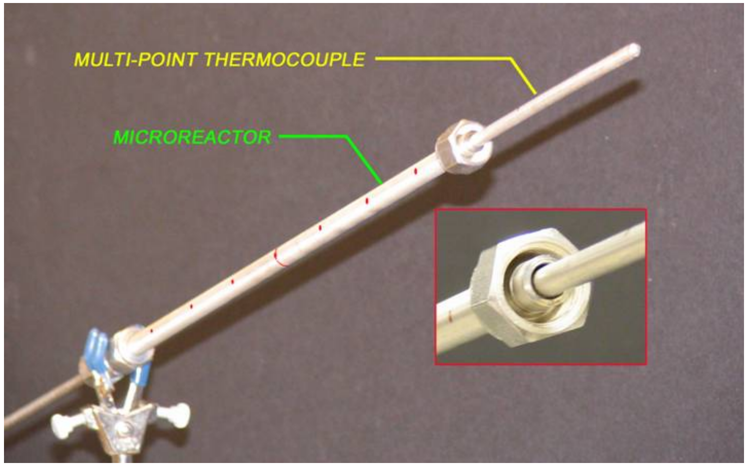


Velocity vectors of N-ethylcarbazole at channel exit



Contours of N-ethylcarbazole symmetry plane

Initial Microchannel Reactor Results



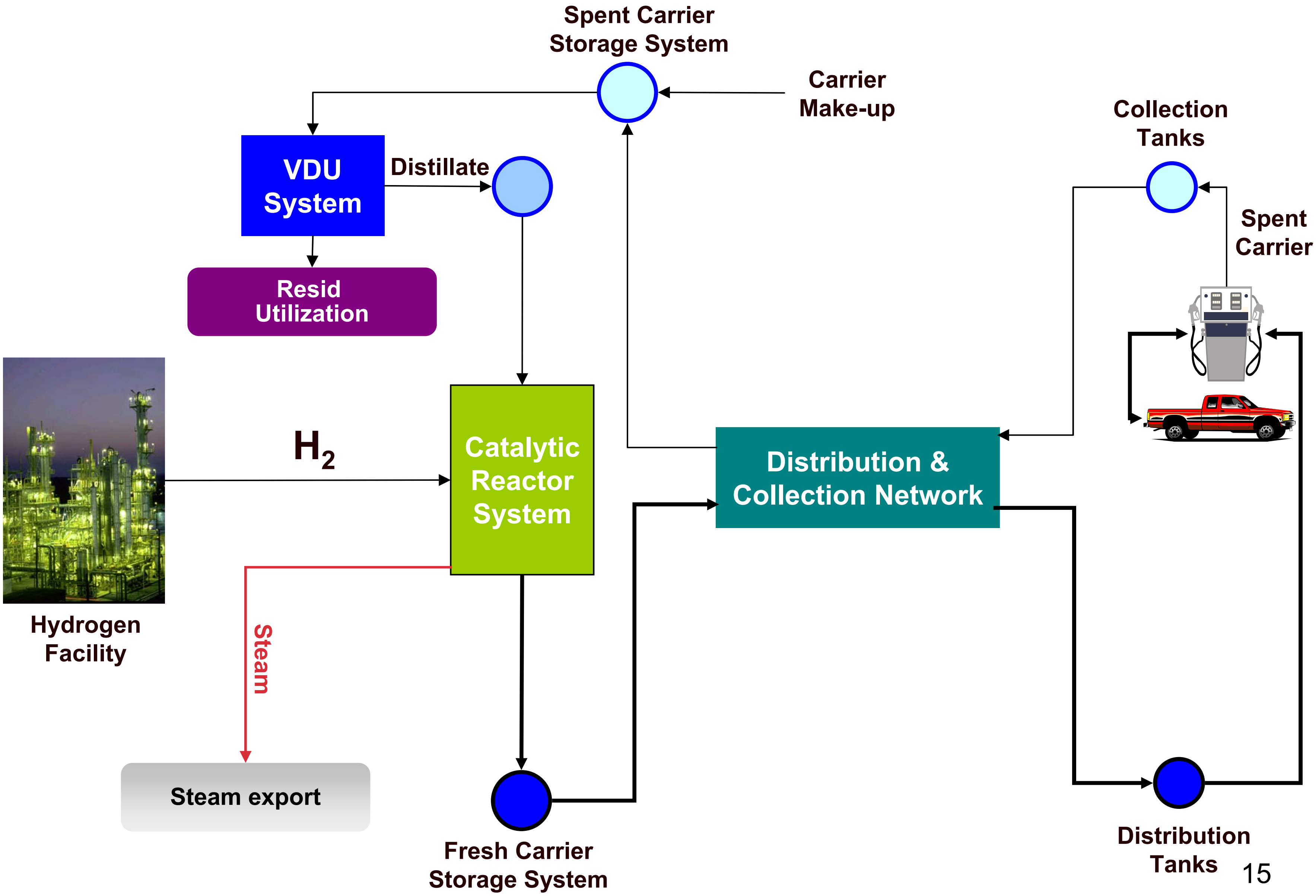
Microchannel Reactor Results.
Reactor Temperature 250 ^{0}C

	Feed Rate (ml/min)	H_2 Flow (sccm)	Conversion (%)
Annular Flow	0.10	11.35	18.85
Channel Flow	0.10	10.59	17.61
Restart after 14 days	0.10	9.67	16.07

- Reactor is isothermal
- Removing thermocouple changed flow pattern but gave same conversion.

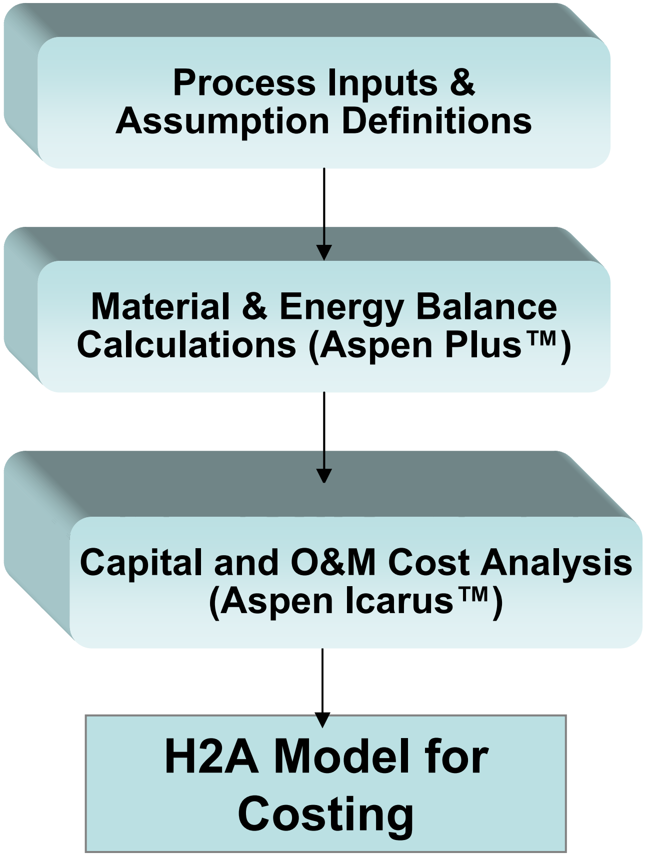
Conclusion: Microchannel reactor remains best candidate for prototype.

Economics: System Overview



Approach: Hydrogenation Economics

- Three scales of hydrogenation throughput were analyzed
  - 20 MMSCFD H2 and 5000 bpd of Product
  - 100 MMSCFD H2 and 24000 bpd of Product
  - 1000 MMSCFD H2 and 240,000 bpd of Product
  - H2A Model used



Process Inputs & Assumption Definitions

Material & Energy Balance Calculations (Aspen Plus™)

Capital and O&M Cost Analysis (Aspen Icarus™)

H2A Model for Costing

APCI Liquid Carrier Economics Summary

- Hydrogenation 0.86-2.5 $/kg
  - Factors
    - Carrier price
    - Storage
    - Carrier loss
- Distribution 0.14 $/Kg
- On-site Dehydrogenation 1.63 $/Kg
    - Compression 0.86 $/Kg
    - Storage 0.52 $/Kg
    - Dispenser 0.04 $/Kg
    - Balance of Station 0.21 $/Kg
- Projected Delivery Cost - $3.4/Kg. ($2.6-$4.3/KG)

Economics: Onboard Upside

- On-board Dehydrogenation eliminates compression from 2 bar to 350 bar
  - Potential to avoid 0.86 $/Kg in compression cost
  - Will eliminate storage of high pressure H2 either on site or on board the FCV
  - Direct supply of H2 from micro-channel reactor to fuel cell at 2 bar
- Needs
  - Validation of design of Micro-channel reactor
  - Autothermal Hydrogen Carrier (STP 25)
  - Understand the cost/possibility of heat integration between PEM fuel cell and micro-channel reactor

Future Work/Milestones

FY ‘08-FY ’09

- Choose reactor configuration for prototype reactor
  - Three candidate reactor to test principles
  - Combine best features of each type
- Define characteristics/parameters for integration
  - UTRC fuel cell
  - OEM automobile
- Build required test facilities

1Q FY ‘10

- Decide on prototype design

Summary

- This projects supports Liquid Carrier by developing a dehydrogenation reactor system for H_2 delivery.
- Packed bed reactor works well, but design limitations limit reactor efficiency.
- Thin-film catalysts (useful for monoliths and microchannel reactor) can be made with high catalyst efficiency.
- Monolith reactors are useable, but flow instabilities will cause design limitations.
- Microchannel reactors still look like most viable alternative.
  - Feed distribution system and channel size/shape parameters will have to be optimized

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